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Photoacoustic Determination of Optical Properties of Aerosol Particles Collected on Filters: Development of a Method Taking into Account Substrate Reflectivity

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16. ABSTRACT

The absorptivity and imaginary index of refraction for carbon and methylene blue particles were inferred from the photoacoustic spectra of samples collected on Teflon filter substrates. Three models of varying complexity were developed to describe the photoacoustic signal as a function of filter loading and sample absorptivity. Model equations were least-squares fitted to the experimental data by an iterative procedure, using the sample absorptivity and the photoacoustic reference (saturation) signal as variables. For PA measurements in the visible wavelength range, the best fit could be obtained with a model including the diffuse reflection of light reaching the filter surface after its first pass through the sample. Using this model the absorptivity of soot at 600 nm was measured as 6.91 ± 0.85 m^2/g (base e). Measurement at 780 nm, 1200 nm and 1600 nm were also made. Using a carbon particle density of 2.0 g/cm^3 the imaginary index of refraction was obtained, indicating a constant index within experimental uncertainty; the value at 600 nm was 1.14 ± 0.14.

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Photoacoustic determination of optical properties of aerosol particles collected on filters: development of a method taking into account substrate reflectivity

R. Röhl, W. A. McClenny, and R. A. Palmer

The absorptivity of soot and methylene blue particles collected on Teflon filters is derived from photoacoustic measurements by least squares fitting a simple expression based on Beer's law to the experimental data. Refinements of the expression take into account the diffuse reflection of light by the filter substrate, yielding a base 10 absorptivity at 600 nm for soot of 3.00 ± 0.37 m^2/g. This value is in close agreement with the result of transmission measurements performed on the same samples (3.08 ± 0.05 m^2/g).

I. Introduction

The optical properties and chemical composition of airborne particles (aerosols) are of considerable interest to workers in the field of air quality research. Since ambient concentrations on a mass/volume basis are usually very low, most analytical techniques require a preconcentration step to bring the species of interest into the detectable range. One preconcentration method under active investigation by the U.S. Environmental Protection Agency involves the separation of particles into two size fractions and their collection on Teflon filters by dichotomous virtual impactor samplers.[1] Nondestructive elemental analyses of these samples for elements with atomic number $Z \geq 13$ are routinely carried out by x-ray fluorescence.

Our research interest is to apply photoacoustic spectroscopy (PAS) to the nondestructive and quantitative determination of molecular species in filter-collected particles. Because the soot present in all ambient samples is very strongly absorbing, we are also concerned with the optical properties of this material and how it affects our photoacoustic (PA) measurements. A review of optical techniques for the measurement of light absorption by airborne particles, for both *in situ* and bulk samples, was recently prepared by Gerber.[2] The First International Workshop on Light Absorption by Aerosol Particles[3] was organized to provide a direct and up-to-date comparison of various methods of measuring aerosol light absorption. We wish to report here some results of PA measurements on filter samples of pure soot and methylene blue particles collected at the workshop.

Three models of varying complexity were developed to describe the PA signal as a function of filter loading and sample absorptivity. Model equations were least squares fitted to the experimental data by an iterative procedure, using the sample absorptivity and the PA reference (saturation) signal as variables. For PA measurements in the visible wavelength range, the best fit could be obtained with a model taking into account the diffuse reflection of light reaching the filter surface after its first pass through the sample. The absorptivity of soot at 600 nm derived from this model is in close agreement with the value determined from transmission measurements using the integrating plate method.[4,5]

II. Experimental

The samples used in this investigation were Teflon filters (Ghia Corp. type 501) loaded with soot from a diffusion flame or with methylene blue aerosol, using a dichotomous virtual impactor sampler at a flow rate of 16.7 liters/min. This type of sampler divides particles into two size fractions, fine (<2.5-μm aerodynamic diam) and coarse (2.5–15-μm aerodynamic diam). Different filter loadings were obtained by varying sampling time between 1 and 10 min. Only the fine fraction filters were analyzed.

For PA measurements, samples were mounted in a specially designed cell (Fig. 1) which accepts intact filters in their slide frames. Spectra extending from 200 to 2000 nm were recorded with an EG&G Princeton

W. A. McClenny is with U.S. Environmental Protection Agency, Environmental Science Research Laboratory, Research Triangle Park, North Carolina 27711; the other authors are with Duke University, Paul M. Gross Chemical Laboratory, Durham, North Carolina 27706.

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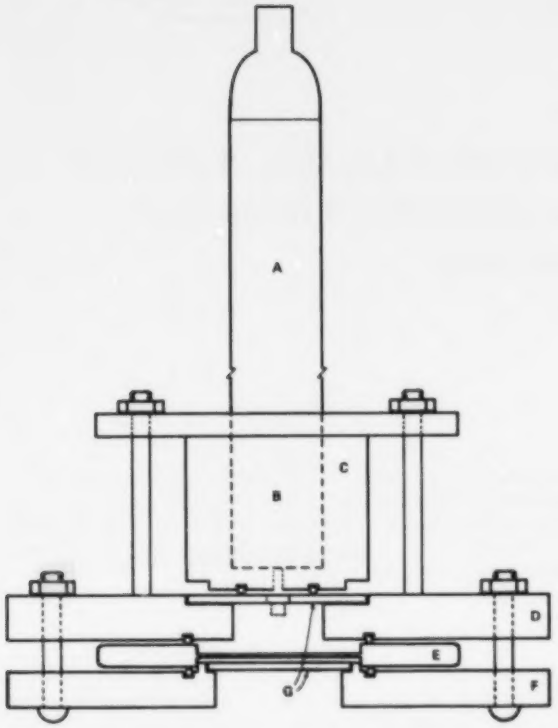

Fig. 1. Composite cross-sectional view of photoacoustic cell: *A*, B&K 2619 preamplifier; *B*, B&K 4165 microphone; *C*, microphone holder; *D*, top plate (aluminum); *E*, Teflon filter and frame; *F*, bottom plate (aluminum); *G*, quartz windows.

Applied Research 6001 PA spectrometer. PA signals were corrected for variations in the xenon arc lamp spectrum by dividing the measured response by the output of a pyroelectric detector illuminated by a small (<10%) but constant fraction of the total beam intensity. A Teflon filter loaded with 2 mg of soot from a propane flame was used to correct for day-to-day variations in detection efficiency. Spectra were recorded at a monochromator slit width of 2 mm, a chopping frequency of 15 Hz, and a scan rate of 100 nm/min.

Determinations of filter reflectivity were also performed with the PAR 6001 spectrometer, using an additional pyroelectric detector (Laser Precision Corp. KT-2230) to measure reflected light.[6] This detector, which produces an ac signal similar to a PA cell, was mounted in a ${}_0R_{45}$ geometry[7] at an approximate distance of 1.5 cm from the illuminated sample surface; it was powered by four 9-V batteries. A reflectance standard was prepared by depositing a 1-mm layer of magnesium oxide smoke onto an aluminum disk of the same diameter as the Teflon filters <1 h prior to analysis and mounting the disk in a slide frame. The reflectivity of this standard was taken to be 98% at all wavelengths investigated (600–1800 nm). Reference and reflectance spectra of blank filters, backed by the quartz window of the PA cell, were recorded at a slit width of 2 mm, a chopping frequency of 20 Hz, and a scan rate of 200 nm/min.

Transmission measurements using the integrating plate method were only made for filters loaded with soot. The apparatus and procedures employed were similar to those described by Lin *et al.*[4] Filters were mounted so that samples faced the illuminating light beam and away from the opal glass integrating plate. Measurements were carried out at 520 nm.

III. Results and Discussion

A. Soot Samples

Spectra of Teflon filters loaded with soot during the Aerosol Light Absorption Workshop exhibited a general decrease of PA response with increasing wavelength (Fig. 2). More detailed analyses were limited to inspection of signals at 600, 780, 1200, and 1600 nm, respectively; the 780-nm wavelength was selected because the spectrometer changes gratings at 800 nm.

Comparison of curves obtained at different soot loadings showed that the PA signal approached saturation at level considerably below the value obtained with the 2-mg reference filter (Figs. 3 and 4). After considering several possible explanations, this observation was attributed to different physical (thermal) properties of the soot on the sample and reference filters. A less dense packing of carbon particles on the reference filter could have been caused by the decrease in flow velocity at higher loading and resulted in an enhanced PA signal.

Since very thick soot samples from the Aerosol Light Absorption Workshop were not available for comparison, appropriate reference levels were estimated from the measured data as described below.

In transmission spectroscopy, the absorptivity of a substance is defined as $a = A/bc$, where A is the absorbance, b the path length of light through a sample, and c the concentration of absorbing material in the sample cell. The absorbance is defined by

$$A = \log I_o/(I_o - I_a), \tag{1}$$

with I_o representing the intensity of the unattenuated light beam and I_a the intensity of the absorbed light. In photoacoustic spectroscopy, I_a corresponds to the signal from a given sample S and I_o to the signal from a blackbody reference R. The PAS analog to absorbance A_{PAS} can therefore be written as

$$A_{PAS} = \log R/(R - S) = \log 1/(1 - S/R). \tag{2}$$

Equation (2) assumes that all absorbed light contributes to the PA signal. This assumption is justified if a low chopping frequency is used in the PA experiment so that the samples are thermally thin. This approach to relating absorbance to PA response is similar to that taken by Vidrine.[8] Identical results can be obtained by solving the idealized 1-D boundary value problem[9] and invoking simplifying assumptions[10] to obtain Eq. (2). Using the definition of absorptivity and a transformation of Eq. (2), one can express the PA signal S as follows:

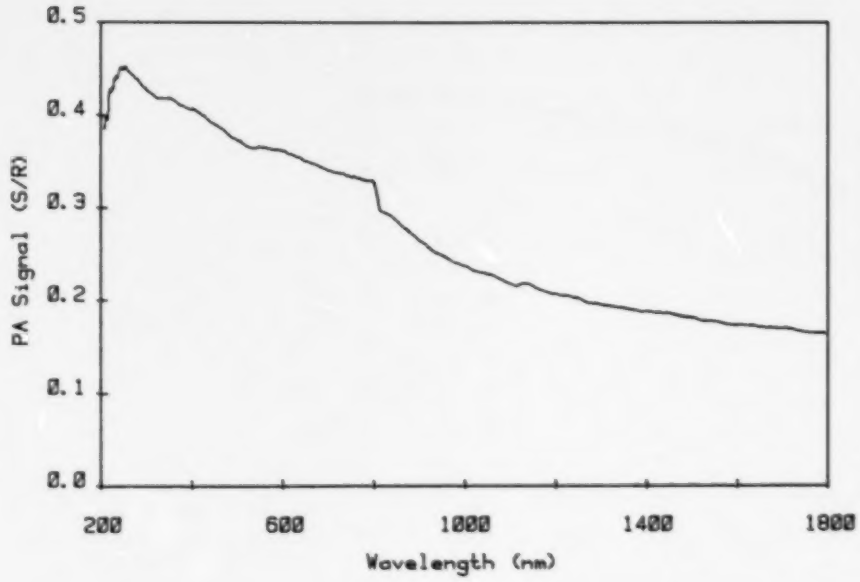

Fig. 2. Photoacoustic signal as a function of wavelength for a typical soot sample. Break at 800 nm is caused by a grating change in the spectrometer.

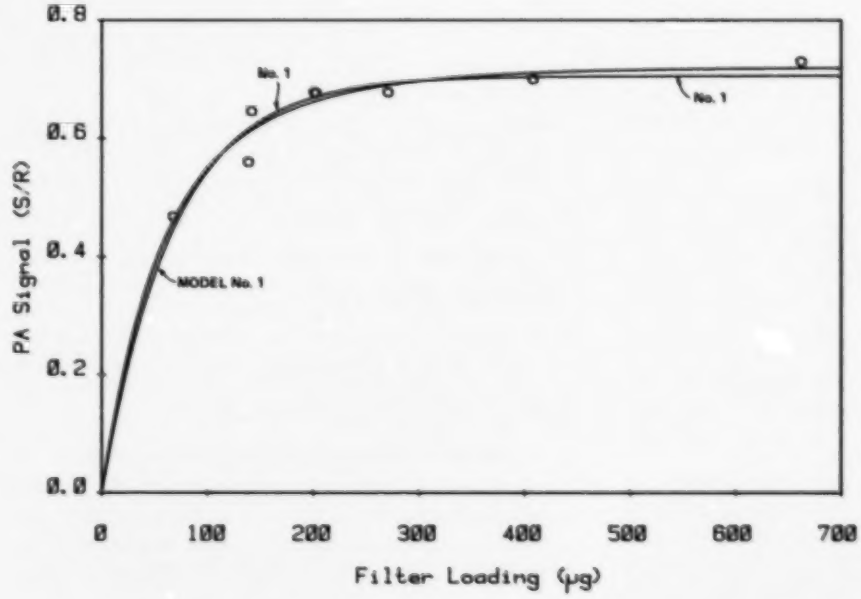

Fig. 3. Photoacoustic signal at 600 nm for soot samples. Solid lines represent least squares fit of two models discussed in the text.

$$S = R(1 - 10^{-abc}). \quad (3)$$

Application of Eq. (3) to the PA analysis of solid materials collected on a filter substrate with the goal of determining absorptivities also requires knowledge of the product bc. A simple derivation shows that this product is given by the loading density of the filter (e.g., in g/m^2).

Assuming that the absorption cell has a thickness b and the same cross-sectional area A' as the light beam, the volume V of the cell is $A'b$. The mass of material within the cell m is the total mass on the filter M, divided by the total filter area A'' and multiplied by A'. The concentration c is then given by $c = m/V = MA'/A''A'b = M/A''b$. Therefore, the product bc is equal to the loading density M/A''. This parameter will henceforth be denoted with the symbol L.

It was initially assumed that the PAS data followed

$$S = R(1 - 10^{-aL}). \quad (4)$$

The two unknowns, R and a, were found by iterative least squares fitting of this equation to the experimental

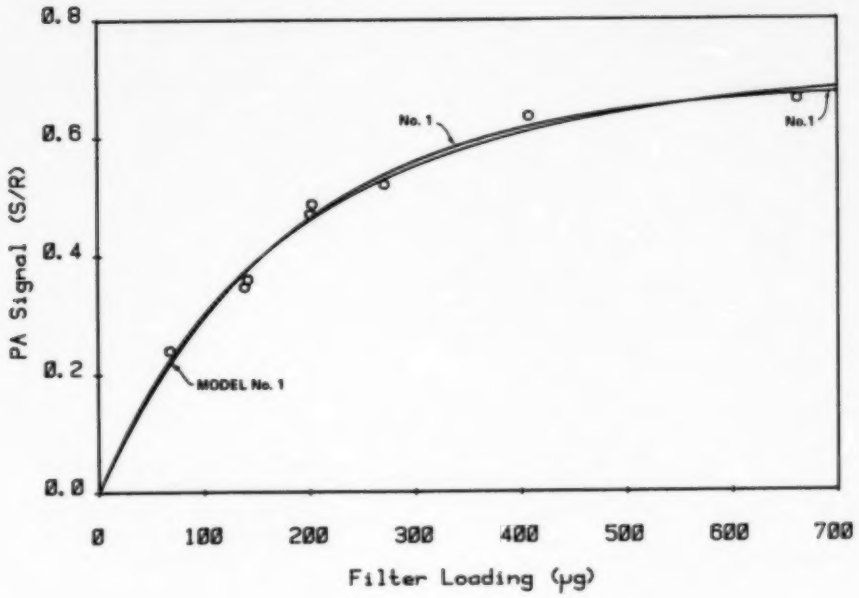

Fig. 4. Photoacoustic signal at 1600 nm for soot samples. Solid lines represent least squares fit of two models discussed in the text.

data points, using R and a as fitting variables. A graphical two-parameter fitting procedure was used to ensure the localization of a unique solution, i.e., an absolute minimum of the chi square.

The uncertainty or standard deviation of the fitted parameters was calculated by the method described by Bevington.[11] Briefly the shape of the function $\chi^2 = f(R,a)$ near the minimum was assumed to be parabolic, and the uncertainty of each parameter was determined by parabolic extrapolation of three points on the $\chi^2(R,a)$ surface near the minimum. The experimental uncertainty at a given wavelength was assumed to be the same for all data points and was estimated from two pairs of near-replicate samples with 140 ± 1- and 200 ± 2-μg soot, respectively.

Results of this analysis for the PA measurements taken at four different wavelengths are listed in Table I. The corresponding best-fitting curves for 600 and 1600 nm are plotted along with the experimental data points in Figs. 3 and 4. Curves obtained with a refined model, which is discussed below, are also shown for comparison. Base 10 absorptivities varied from 1.87 ± 0.08 m^2/g at 1600 nm to 5.18 ± 0.71 m^2/g at 600 nm. Values for the imaginary part of the refractive index were calculated using the formula $n_2 = a\rho\lambda/4\pi$ and are given for base e only in keeping with standard usage. Work published by Jennings *et al.*[12] suggests that n_2 values for aerosols derived from the above formula underestimate n_2 by an amount depending on the particle size distribution and the wavelength of light. Hence these values should be used with caution. The relative standard deviation of the fitted absorptivities was higher at shorter wavelengths because most samples were close to the saturation level (Fig. 3).

B. Methylene Blue Samples

Photoacoustic spectra of methylene blue collected on Teflon filters showed a signal maximum at 710 nm (Fig. 5). The analysis described in the preceding section was applied to PA measurements for five filters loaded at the Aerosol Light Absorption Workshop with 170–659 μg of methylene blue. Again a close fit of Eq. (4) to the experimental data at 710 nm was possible. The derived absorptivity was 0.773 m^2/g using base 10 and 1.78 m^2/g using base e. Since no replicate samples were available, the uncertainty of this value could not be calculated. However, judging from the goodness of fit, the relative standard deviation should be <10%.

C. Error Sources and Refinement of Fitting Model

Only a portion of the filters loaded during the Aerosol Light Absorption Workshop was analyzed mainly due to the difficulties in obtaining accurate sample weights. In addition to the errors in weight determinations and

Table I. Summary of Results for Carbon Particles

Wavelength (nm)	PAS reference $R \pm \sigma_R$	Absorptivity $a \pm \sigma_a$ (m^2/g)	Imag. index of refraction n_2[a]
600	0.696 ± 0.008	5.18 ± 0.71	
		11.9 ± 1.64[b]	1.14 ± 0.16[b]
780	0.687 ± 0.009	3.73 ± 0.36	
		8.59 ± 0.83[b]	1.07 ± 0.10[b]
1200	0.736 ± 0.004	2.54 ± 0.08	
		5.85 ± 0.18[b]	1.12 ± 0.04[b]
1600	0.703 ± 0.004	1.87 ± 0.08	
		4.31 ± 0.18[b]	1.10 ± 0.05[b]

[a] Assuming a particle density of 2.0 g/cm^3 and using the formula $n_2 = a\rho\lambda/4\pi$.
[b] Base e.

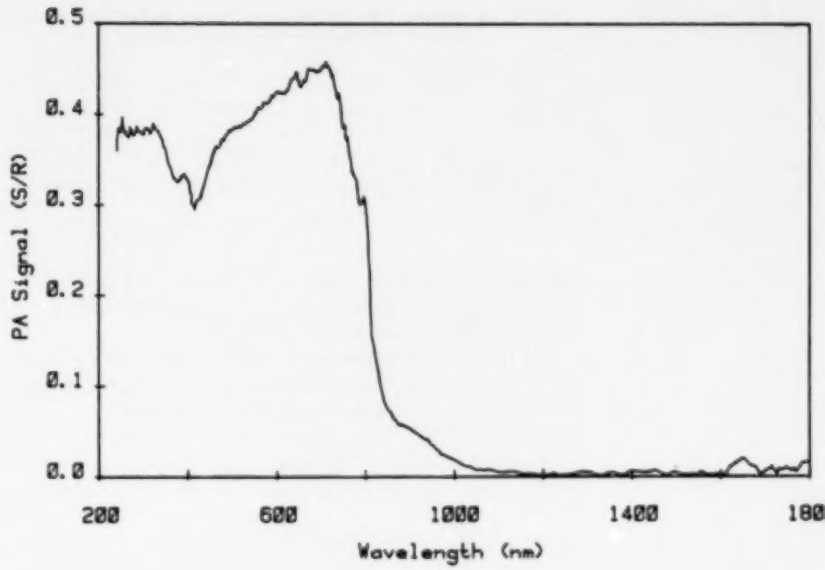

Fig. 5. Photoacoustic signal as a function of wavelength for a typical methylene blue sample.

PA measurements (which were assumed to be random), the calculated absorptivities may be subject to several types of systematic error. Since soot tends to form larger particles by aggregation, the surface coverage at low loadings is heterogeneous. Nonuniform surface coverage in turn leads to reduced light absorption compared with the uniform deposit assumed in the derivation of Eq. (4). Transmission measurements, briefly discussed below, showed that this effect was negligible for the range of loadings investigated in this study. Another type of systematic error is also expected to be most prominent at low loading levels but with an opposing effect on apparent absorptivities. The analogy to transmission spectroscopy assumes that light passes a sample only once, i.e., that light not absorbed during the first pass is lost by transmission through the filter. However, since Teflon filters reflect a significant portion of the light impinging on their surface, the absorption length is increased, thus increasing the apparent absorptivity.

To refine our estimates of sample absorptivities, we measured the reflectivity of blank Teflon filters relative to a freshly prepared magnesium oxide standard. At 600 nm we found a relative reflectivity F of 0.55 ± 0.02 for unsupported filters and a value of 0.58 ± 0.02 when the same filters were backed by the quartz window of the PA cell. Results of measurements with the window backing at several wavelengths are plotted in logarithmic form in Fig. 6.

The first refinement applied to the fitting calculations discussed previously (model 1) was to assume that $F \times 100\%$ of the light reaching the filter surface was reflected back through the sample, again in a straight line. Equation (5) describes the PA signal as a function of loading L when these assumptions apply (model 2):

$$S = R(1 - 10^{-aL}) + RF10^{aL}(1 - 10^{-aL}). \quad (5)$$

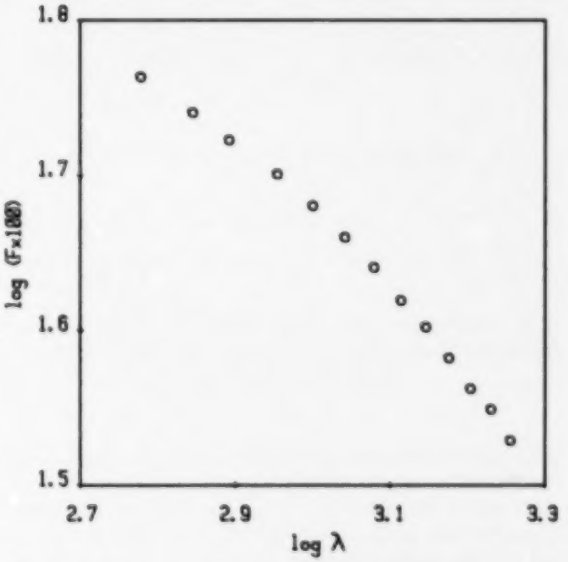

Fig. 6. Logarithm of filter reflectivity F (in percent) vs logarithm of wavelength (in nanometers). The reference, consisting of fresh magnesium oxide smoke, was assumed to be 98% reflective.

This model was further refined by taking into account that Teflon filters reflect light diffusely and not straight back through the sample. This leads to an increased effective path length, which depends on the angular intensity distribution $I_r(\vartheta)$ of the reflected light. For a perfect diffuse reflector, this distribution is described by Lambert's cosine law[7]

$$I_r(\vartheta) = B \cos\vartheta. \quad (6)$$

In Eq. (6), ϑ is the angle between the incident light

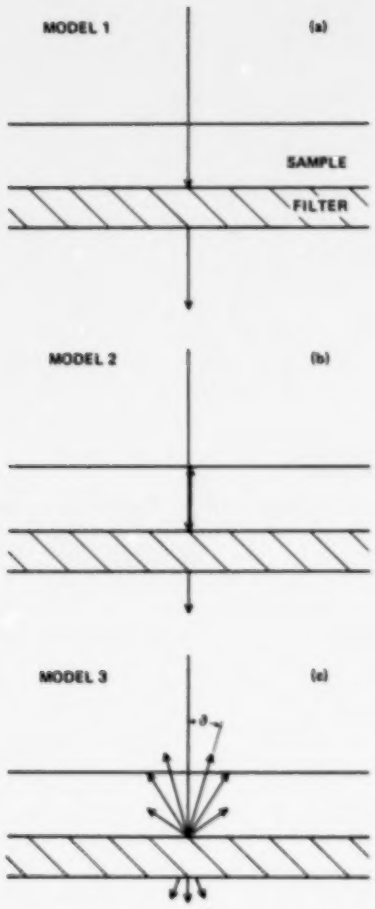

Fig. 7. Illustration of three models used to fit PAS data: (a) simple transmission model; (b) model with mirror reflections at filter surface; (c) diffuse reflection model.

beam (perpendicular to the planar sample surface) and the direction of observation, and B is a constant proportional to the intensity of the illuminating light beam. The effective path length of reflected light through a layer of thickness b is given by $b/\cos\vartheta$. Weighting this path length with the angular intensity distribution given by Eq. (6) and integrating over all possible angles (0–90°) yield the average effective path length b':

$$b' = \int_0^{\pi/2} \cos\vartheta(b/\cos\vartheta)d\vartheta = \int_0^{\pi/2} bd\vartheta = b\pi/2. \quad (7)$$

With this second refinement, the PA response as a function of loading is given by Eq. (8) (model 3):

$$S = R(1 - 10^{-aL}) + RF10^{-aL}(1 - 10^{-aL\pi/2}). \quad (8)$$

For reference purposes, the three different models fitted to the experimental PAS data are summarized in Fig. 7. Results obtained for the PA measurements on soot at 600 nm with all three models are compared in Table II. Calculations with model 3 for the other wavelengths investigated, namely, 780, 1200, and 1600 nm, were 2.31 ± 0.11, 1.66 ± 0.05, and 1.27 ± 0.03 m^2/g, respectively; the absorptivity of methylene blue at 710 nm was determined to be 0.465 m^2/g.

Table II. Absorptivity of Soot at 600 nm as Determined by Three Different Methods of Fitting the Experimental PAS Data [a]

Model	Equation	$\chi^2 \times 10^5$	$a_{10} \pm \sigma(m^2/g)$	$a_e \pm \sigma(m^2/g)$
1	4	513	5.18 ± 0.71	11.9 ± 1.64
2	5	462	3.45 ± 0.41	7.95 ± 0.94
3	8	445	3.00 ± 0.37	6.91 ± 0.85

[a] Note that χ^2 decreases with increasing refinement of the fitting model.

Since the refinements of the initially used simple model increase the assumed path length of light through a sample, they decrease the apparent absorptivity of the sample material. The values calculated from model 1 to model 3 for soot at 600 nm are in the ratios 1.0:0.67:0.58. Very similar ratios (1.0:0.67:0.57) were obtained when a test data set was calculated from model 3 and fitted with the equations of models 1 and 2. The results in Table II may also be compared to the absorptivity derived from transmission measurements with the integrating plate method which were performed on five of the soot samples analyzed by PAS. A base 10 absorptivity of 3.55 ± 0.06 m^2/g was obtained at 520 nm. This corresponds to 3.08 ±0.05 m^2/g at 600 nm if the imaginary part of the refractive index of soot is assumed to be constant[13] between 520 and 600 nm. The latter value is in close agreement with the absorptivity calculated from model 3. An additional comparison can be made with the results of *in situ* PA measurements on acetylene smoke reported by Roessler and Faxvog.[14] These authors found a base e absorptivity of 8.3 ± 0.9 m^2/g at 514.5 nm. With the aforementioned assumption of constant n_2, this translates into a base 10 absorptivity at 600 nm of 3.09 ± 0.34 m^2/g.

Based on the results of this study, we conclude that PA measurements on thin, strongly absorbing samples supported by filter membranes can be described by an expression analogous to Beer's law, which takes into account the diffuse reflection of light at the surface of the sample substrate. Fitting this expression to the experimental data can serve to estimate absorptivities. When strongly light-scattering samples are to be analyzed, further refinements of the model may be necessary.

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